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REGULAR ARTICLE

Spectroscopy and dissociation of I_2–Rg (Rg = Kr and Xe) van der Waals complexes

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Abstract The spectroscopy and dissociation of I_2–Rg (Rg = Kr and Xe) van der Waals complexes have been studied in detail using MP2 and CCSD(T) methods in conjunction with the correlation-consistent triple-ζ and quadruple-ζ quality basis sets. The large-core Stuttgart–Dresden–Bonn (SDB) relativistic pseudopotential is used for all heavy elements. The dissociation energy and depth of the potential well have been calculated using potential method and supermolecular approach in order to remove the discrepancy among the existing theoretical and experimental values. Most of the spectroscopic properties are first reported, and the rest agree very well with the theoretical and experimental values wherever available.

Keywords Dissociation energy · Depth of the potential well · Spectroscopic constants · MP2 method · CCSD(T) method · Rg–I_2 van der Waals complexes

1 Introduction

The iodine rare-gas van der Waals complexes have been extensively studied by experiments. The majority of these works concentrated on the lighter rare-gas systems (I_2–Rg, where Rg = He, Ne, Ar) with the main emphasis on the I_2–Ar complex. In contrast, very little work has been carried out on the van der Waals complexes I_2–Kr and I_2–Xe containing heavier rare-gas. Between these two complexes, the I_2–Xe complex has been the subject of main concern because of contradictory reports from various theoretical and experimental groups on the depth of the potential well and dissociation energy. Randall and Donaldson [1] studied the photo-physics and photo-chemistry of I_2 in rare-gas clusters and determined potential parameters of I_2–Rg (Rg = Ar, Kr, Xe) complexes. They reported the depth of the potential of the linear isomer of I_2–Xe complex is about 195 cm^{-1}. Li and Thomson [2, 3] adopted non-equilibrium molecular dynamics (NEMD) simulation and non-equilibrium mixed quantum–classical (MQC) surface-hopping approach to calculate the potential parameters of the I_2–Xe complex. They also developed a potential function based on *ab initio* calculation for using it in molecular dynamics simulations of the vibrational relaxation of I_2 in xenon. The calculated value of the depth of the potential is 36 cm^{-1} higher than the experimental value of Randall and Donaldson. Kiviniemi et al. [4, 5] carried out time-resolved coherent anti-stokes Raman-scattering (CARS) measurements to study the interaction between xenon atom and iodine molecule in solid krypton matrix. In support of the experimental work, they performed molecular dynamics and wave packet simulations in order to distinguish different structures of the complex and to produce the CARS signals. The predicted dissociation energy for the linear isomer of I_2–Xe complex was 285 cm^{-1}. They also determined I–I stretching frequency (ω_3) and anharmonic constant ($\omega_3 x_e$). The I–I stretching frequency is lower than the earlier experimental value of Böhling et al. [6]. In order to remove the discrepancy between various experimental and theoretical values, and to predict the potential parameters very accurately, we have studied, in detail, the potential parameters and spectroscopic constants of the I_2–Xe complex along with the I_2–Kr van der Waals complex.

To understand the large difference between theoretical and experimental values for the dissociation energies, the zero-point energy (ZPE) corrected and uncorrected

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dissociation energies, D_0 and D_e, have been calculated using potential method as well as supermolecular approach. D_e is the depth of the potential well of the van der Waals complexes. The method and computational details are described in Sect. 2 followed by a discussion of the results in Sect. 3.

2 Method and computational details

We consider the following potential for the I_2–Rg van der Waals complexes

$$V(r_1, r_2, \theta) = \frac{1}{2} f_{11} (\Delta r_1)^2 + \frac{1}{2} f_{\theta\theta} (\Delta\theta)^2 + \frac{1}{2} f_{22} (\Delta r_2)^2 + f_{111} (\Delta r_1)^3 + \cdots \quad (1)$$

where Δr_1 is the stretching of the weak Rg–I van der Waals bond, r_1 at equilibrium, Δr_2 is the stretching of the I–I bond, r_2, $\Delta\theta$ is the valence angle bending from an assumed linear equilibrium position, f_{11}, f_{22} and $f_{\theta\theta}$ are the stretching van der Waals harmonic force constant, free I–I bond stretching force constant and bending force constant, respectively. The van der Waals anharmonic stretching or cubic force constant is denoted by f_{111}.

The interacting potential of van der Waals complexes, which is composed of a short-range repulsive term arising from the overlap of closed-shell orbitals and the long-range attractive contribution with a radial dependence, can be represented by the Lennard–Jones (L–J) potential [7].

$$V(r) = \varepsilon \left(\left(\frac{r_e}{r} \right)^{12} - 2 \left(\frac{r_e}{r} \right)^{6} \right) \quad (2)$$

where ε is the depth of the potential well of the complexes and r_e is the equilibrium separation distance at which $V(r)$ is minimum. Generally, r_e is the van der Waals equilibrium bond distance between Rg atom and I atom for linear complexes and between Rg atom and the centre of mass of I_2 molecule for T-shaped complexes. The linear and T-shaped isomers are shown in Figs. 1 and 2, respectively. For linear complex, r_1 is same as r_e, but for T-shaped complex r_1 is different from r_e. The depth of the potential well (ε) is the ZPE uncorrected dissociation energy (D_e) of the complex. Expanding the expression for L-J (6, 12) potential of (2) in Taylor series, we get

$$V(r) = -\varepsilon + \frac{36}{r_e^2} \varepsilon (r - r_e)^2 - \frac{252\varepsilon}{r_e^3} (r - r_e)^3 + \frac{1,113}{r_e^4} (r - r_e)^4 + \cdots \quad (3)$$

Fig. 1 Linear isomer of I_2–Rg van der Waals complex

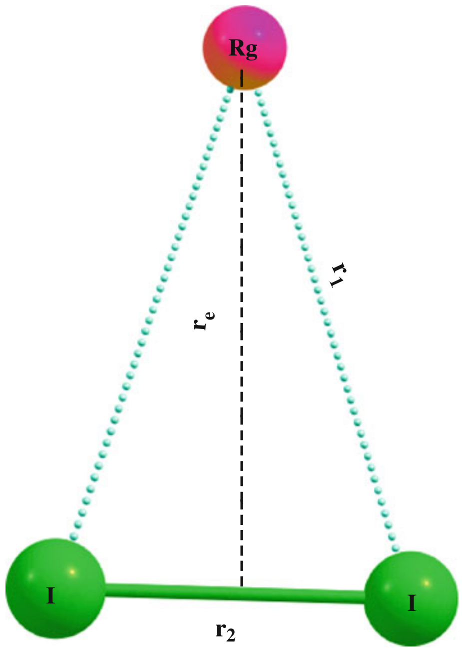

Fig. 2 T-shaped isomer of I_2–Rg van der Waals complex

Comparing (1) and (3), we get

$$\frac{1}{2} f_{11} = \frac{36\varepsilon}{r_e^2} \quad \text{or} \quad \varepsilon = \frac{r_e^2 f_{11}}{72} \quad \text{and} \quad f_{111} = -\frac{252\varepsilon}{r_e^3} = -\frac{252 f_{11}}{72 r_e} \quad (4)$$

Using the expressions in (4), we can calculate the depth of the potential well and the van der Waals anharmonic stretching or cubic force constant. In the above calculation, the variation of r is considered for a fixed r_2(I–I) distance.

The relation between D_j and the rotational constant B of a tri-atomic complex having stretching frequencies is given by

$$D_j = 4B^3 \left(\left(\frac{\zeta_{23}^2}{\omega_1^2} \right) + \left(\frac{\zeta_{21}^2}{\omega_3^2} \right) \right) \quad (5)$$

where ζ_{23} and ζ_{21} are Coriolis coupling constants and D_j is centrifugal distortion constant [8].

Among three frequencies, ω_2 is the bending frequency and ω_1 and ω_3 are two linear stretching frequencies, such that ω_1 is van der Waals weakly stretching Rg–I frequency for linear complexes and weakly stretching between Rg atom and centre of mass of I_2 molecule for T-shaped complexes and ω_3 is the I–I stretching frequency.

The MP2 [9] and CCSD(T) [10, 11] methods are applied to calculate the spectroscopic parameters of the complexes. The MP2 is the second order Møller–Plesset perturbation theory which includes double excitations, and CCSD(T) method includes singles and double excitations and an estimate of triple excitations by a perturbative treatment.

The spectroscopic constants D_j, ω_3x_e, ζ_{23}, ζ_{21} and ζ_{31} are calculated at MP2 level and others such as equilibrium bond distances (r_1, r_2, r_e, r_{cm}), frequencies (ω_1, ω_2, ω_3), force constants (f_{11}, f_{22}, $f_{\theta\theta}$, f_{111}) and rotational constant (B), well depth (D_e or ε) and dissociation energy (D_0) are calculated both at MP2 and CCSD(T) levels. Using the values for ζ_{23}, ζ_{21}, B, ω_1, and ω_3 in (5), the centrifugal distortion constant D_j is calculated. The depth of the potential well (ε or D_e) of the complexes is calculated at these two levels also using the potential method discussed above and the supermolecular approach.

In the supermolecular approach, the depth of the potential well or ZPE uncorrected dissociation energy (D_e) of the complex can be written as

$$D_e = E_{I_2\mathrm{Rg}} - E_{\mathrm{BSSE}} - E_{\mathrm{Rg}} - E_{I_2} + E'_{\mathrm{BSSE}} \tag{6}$$

where E_{I_2Rg}, $E_{Rg}$and $E_{I_2}$are the energies of I_2–Rg, Rg, and I_2, respectively. The correction, E_{BSSE}, for the I_2–Rg complexes and the correction, E'_{BSSE}, for the fragmented molecule I_2 due to the basis-set superposition error (BSSE) are estimated using the counterpoise method of Boys and Bernardi [12]. To correct BSSE, each atom is considered as a fragment. The BSSE correction for the complexes is about 400 cm^{-1} and that for I_2 molecule is about 350 cm^{-1}. The deformation energy of I_2 is not taken into account in the calculation as this energy is very small. The depth of the potential calculated by potential method and supermolecular approach is denoted by D_e^p and D_e^s, and the dissociation energy is denoted by D_0^p and D_0^s.

Two basis sets are employed to check the consistency of the calculated potential parameters and spectroscopic constants. The correlation-consistent valence triple-ζ and quadruple-ζ basis sets, cc-pVTZ and cc-pVQZ are used with the large-core Stuttgart–Dresden–Bonn (SDB) [13] relativistic pseudopotential [14] for all atoms of the I_2–Rg van der Waals complexes. The SDB-cc-pVTZ and SDB-cc-pVQZ basis sets in conjunction with a core polarization potential (CPP) render excellent agreement with experiment for compounds of the later heavy p-block elements [13]. Effective core potentials (ECPs) [14] not only replace the core electrons in a calculation with an effective potential but also eliminate the need for the core basis functions, which usually require a large set of Gaussians to describe them. Effective core potentials (ECPs), in addition to replacing the core, are used to represent relativistic effects, which are largely confined to the core. In this context, both the scalar (spin-free) relativistic effects and spin–orbit (spin-dependent) relativistic effects are included in effective potentials [13]. As Kr and Xe are closed-shell systems, the SDB-cc-pVQZ [13] basis set is reduced by eliminating 1f (0.44286) from the basis set of Kr and 1f (0.325564) from the basis set of Xe. The composition of basis sets is as follows:

BS1 = I: SDB-cc-pVTZ & Rg (Kr, Xe): SDB-cc-pVTZ
BS2 = I: SDB-cc-pVQZ & Rg (Kr, Xe): SDB-cc-pVQZ -1f

The above basis sets do not contain diffuse functions. Addition of diffuse functions makes the systems more bound which is unphysical.

The GAUSSIAN 03 suite of quantum chemistry program [15] is used for *ab initio* molecular orbital calculations. The Coriolis coupling constants (ζ_{23}, ζ_{21}, and ζ_{31}), frequencies (ω_1, ω_2, and ω_3) and ω_3x_e are obtained directly from the GAUSSIAN 03 program.

3 Results and discussion

The ground-state energies for linear and T-shaped isomers of these complexes are calculated at CCSD(T)/BS2 level to analyze the stability of the two isomers. Between two isomers, the linear isomers of I_2–Kr and I_2–Xe are more stable than their T-shaped isomers. The energy difference between linear and T-shaped isomers for I_2–Kr complex is about 29.63 cm^{-1} and that for the I_2–Xe complex is about 58.14 cm^{-1}. The stability of the linear isomer increases when complex becomes heavier. The structures for linear and T-shaped isomers of these van der Waals complexes are shown in Figs. 1 and 2, respectively.

The potential parameters and spectroscopic constants of the linear I_2–Kr van der Waals complex are summarized in Table 1 along with the experimental values for comparison. The equilibrium bond length between iodine and krypton atom, r_1 (I–Kr) is consistent with the experimental value of Randall and Donaldson [1]. The distance between the Kr atom and the centre of mass of iodine molecule, r_{cm} also agrees within 0.05 Å with the experimental values of Kiviniemi et al. [4]. The I–Kr equilibrium bond length (r_1) increases about 0.13 Å from MP2/BS2 to CCSD(T)/BS2, but the binding energy (D_0) decreases about 100 cm^{-1} from MP2 to CCSD(T). We have calculated the depth of the potential and dissociation energy in two ways, D_e^p and D_0^p are calculated using potential method, the expression for ε is deduced in (4) and D_e^s and D_0^s are estimated by supermolecular approach given in (6). The binding energy (D_0^p) obtained by potential method at CCSD(T)/BS2 level deviates very little, about 9 cm^{-1} from the recent experimental value of Kiviniemi et al. [4]. The dissociation energy calculated by the supermolecular approach is about 17 cm^{-1} greater than the experimental value [4]. In between these two methods, the dissociation energy obtained by potential method agrees better with the experimental value. The depth of the potential well (D_e) estimated by two methods is much higher than the experimental value of Randall and Donaldson. The difference

Table 1 Spectroscopic properties of linear isomer of I_2–Kr van der Waals complex in its ${}^1\Sigma_g^+$ ground state

Spectroscopic properties	Method/Basis set				Others
	MP2/BS1	MP2/BS2	CCSD(T)/BS1	CCSD(T)/BS2	Expt.
r_1 (I–Kr) (Å)	3.816	3.750	3.958	3.880	3.72[a]
r_2 (I–I) (Å)	2.680	2.666	2.708	2.888	
r_{cm} (Å)	5.156	5.083	5.312	5.324	5.37[b]
D_0^p (cm^{-1})	272.5	338.1	265.3	215.4	206[b]
D_0^s (cm^{-1})	238.9	278.3	257.4	188.7	
D_e^p (cm^{-1})	406.4	475.9	387.8	343.2	159.5[a]
D_e^s (cm^{-1})	372.8	416.1	379.9	316.4	
B (cm^{-1})	0.00791	0.0081	0.00751	0.00773	
D_j (10^{-9} cm^{-1})	2.12	3.6			
ω_1 (cm^{-1})	27.2	29.9	21.7	24.6	
ω_2 (cm^{-1})	13.9	15.2	11.1	21.4	
ω_3 (cm^{-1})	226.6	230.4	212.3	218.4	217.3[c]
$\omega_3 x_e$ (cm^{-1})	0.906	0.922			0.77[c]
f_{11} (mdyne/Å)	0.0399	0.0484	0.0354	0.0326	
$f_{\theta\theta}$ (mdyne Å)	0.0134	0.0161	0.0085	0.0106	
f_{22} (mdyne/Å)	3.8389	3.9679	3.3709	3.5663	
f_{111} (mdyne/$Å^2$)	–0.03659	–0.042	–0.02246	–0.0294	
ζ_{23}	0.88846	0.88662			
ζ_{21}	–0.4586	–0.46222			
ζ_{31}	–0.01812	–0.01691			

[a] Ref. [1], [b] Ref. [4], [c] Ref. [6]

between D_e and D_0 is the zero-point energy (ZPE) of the complex which is about 128 cm^{-1}. If ZPE is added to the value 206 cm^{-1} of Kiviniemi et al., the value of D_e will be about 334 cm^{-1} which differs about 9 cm^{-1} from our D_e^p value obtained by potential method. The calculated values for the harmonic vibrational frequency ω_3 and anharmonicity constant ($\omega_3 x_e$) reproduce the experimental values of Böhling et al. [6]. The rest of the spectroscopic constants improve consistently with respect to method and basis set, and the best results, predicted for the first time, are obtained at CCSD(T)/BS2 level.

Table 2 compares the potential parameters of the T-shaped isomer of I_2–Kr van der Waals complex with the experimental values of Kiviniemi et al. [4], who reported only equilibrium bond length and depth of the potential well. As seen from the Table, the CCSD(T)/BS2 equilibrium bond length (r_e), which is the distance between the centre of mass of I_2 molecule and Kr atom, deviates about 0.14 Å from the experimental value. It may be noted that the value of r_e increases about 0.1 Å from MP2/BS2 to CCSD(T)/BS2. Between the two estimated values for the depth of the potential well, the value (D_e^s) obtained by supermolecular approach agrees better, within 2 cm^{-1} with the recent experimental value of Kiviniemi et al. [4] than that (D_e^p) calculated by potential method. To get an idea about the experimental value for the dissociation energy of the complex, the ZPE, about 128 cm^{-1}, would be subtracted from the experimental value, 289 cm^{-1} of Kiviniemi et al. for the well depth. The approximate experimental value, 161 cm^{-1} estimated in this way is very close, within 2 cm^{-1} to our value for D_0^s calculated using supermolecular approach. For this isomer, the supermolecular approach gives better results than the potential method. The other spectroscopic constants do not change much with the improvement of method and basis set, and our best estimates are obtained at CCSD(T)/BS2 level. These spectroscopic constants are first reported.

The results for linear I_2–Xe van der Waals complex are displayed in Table 3 along with the theoretical and experimental values for comparison. Both the equilibrium bond lengths r_1 (I–Xe) and r_2 (I–I) are in harmony with the existing theoretical and experimental values. For the equilibrium bond length r_{cm}, the difference between the CCSD(T)/BS2 and the recent experimental value of Kiviniemi et al. [4] is about 0.03 Å. The dissociation energies (D_0) calculated by two methods at CCSD(T)/BS2 level are almost equal and these values are very close, about 3 cm^{-1}, to the experimental value of Kiviniemi et al. The depth of the potential well obtained by two methods is much higher than the molecular dynamics simulation value of Li and Thompson [3]. This difference arises from both method and basis set used in the calculation of Li and Thompson who carried out single-point energy calculation at MP2 level using 6-311G basis set for iodine and double-ζ quality basis set for xenon atom. Both method and basis set used in our calculation are much better than those employed by Li

Table 2 Spectroscopic properties of T-shaped isomer of I_2–Kr van der Waals complex in its $^1\Sigma_g^+$ ground state

Spectroscopic properties	Method/basis set				Others
	MP2/BS1	MP2/BS2	CCSD(T)/BS1	CCSD(T)/BS2	Expt.
r_1 (I–Kr) (Å)	4.356	4.285	4.504	4.404	
r_2 (I–I) (Å)	2.678	2.663	2.706	2.687	
r_e (Å)	4.146	4.073	4.295	4.194	4.05[a]
D_0^p (cm^{-1})	185.4	177.4	182.7	176.1	
D_0^s (cm^{-1})	181.3	226.9	172.9	159.0	
D_e^p (cm^{-1})	318.4	293.5	304.5	303.8	289[a]
D_e^s (cm^{-1})	314.3	365.0	294.7	286.7	
B (cm^{-1})	0.01554	0.01611	0.01448	0.01516	
D_j (10^{-8} cm^{-1})	2.18	1.80			
ω_1 (cm^{-1})	22.1	25.6	17.5	21.4	
ω_2 (cm^{-1})	16.9	19.2	13.6	15.7	
ω_3 (cm^{-1})	227.2	231.2	212.4	218.5	
$\omega_3 x_e$ (cm^{-1})	1.59	1.62			
f_{11} (mdyne/Å)	0.0265	0.0253	0.0236	0.0247	
$f_{\theta\theta}$ (mdyne Å)	0.0191	0.0247	0.0124	0.0166	
f_{22} (mdyne/Å)	3.8593	3.9977	3.3738	3.5705	
f_{111} (mdyne/Å^2)	–0.0224	–0.0303	–0.0135	–0.0206	
ζ_{23}	0.83983	0.83657			
ζ_{21}	–0.54284	–0.54785			
ζ_{31}	0	–0.00158			

[a] Ref. [4]

Table 3 Spectroscopic properties of linear isomer of I_2–Xe van der Waals complex in its $^1\Sigma_g^+$ ground state

Spectroscopic properties	Method/basis set				Others	
	MP2/BS1	MP2/BS2	CCSD(T)/BS1	CCSD(T)/BS2	Expt.	Theor.
r_1 (I–Xe) (Å)	3.909	3.847	4.065	4.008		3.94[a], 3.88[b]
r_2 (I–I) (Å)	2.681	2.668	2.708	2.689		2.667[a], 2.667[c]
r_{cm} (Å)	5.250	5.181	5.419	5.352	5.38[d]	
D_0^p (cm^{-1})	450.2	483.5	290.7	277.7	285[d]	
D_0^s (cm^{-1})	464.8	380.3	286.3	281.6		
D_e^p (cm^{-1})	584.5	620.9	390.5	404.4	194.8[b]	225[c]
D_e^s (cm^{-1})	599.1	517.7	409.2	408.2		
B (cm^{-1})	0.00592	0.00606	0.00559	0.00572		
D_j (10^{-10} cm^{-1})	9.82	9.54				
ω_1 (cm^{-1})	26.7	28.0	21	21.7		
ω_2 (cm^{-1})	16.2	17.6	12.7	13.8		
ω_3 (cm^{-1})	225.6	229.1	211.9	217.8	210.36 ± 0.02[d], 213.9[e] 210.36 ± 0.04[f]	
$\omega_3 x_e$ (cm^{-1})	0.678	0.687			0.637[d], 0.67[e] 0.636 ± 0.003[f]	
f_{11} (mdyne/Å)	0.0547	0.0600	0.0358	0.0360		
$f_{\theta\theta}$ (mdyne Å)	0.0198	0.0232	0.0121	0.0143		
f_{22} (mdyne/Å)	3.8063	3.9235	3.3597	3.5471		
f_{111} (mdyne/Å^2)	–0.0489	–0.0546	–0.0308	–0.0314		
ζ_{23}	0.91701	0.91512				
ζ_{21}	–0.39804	–0.40237				
ζ_{31}	–0.02574	–0.02582				

[a] Ref. [3], [b] Ref. [1], [c] Ref. [2], [d] Ref [4], [e] Ref. [6], [f] Ref. [5]

and Thompson. The experimental value of Randall and Donaldson is much lower. In fact, in all cases, the experimental values of Randall and Donaldson are consistently much lower. In the work of Randall and Donaldson, the Rg–I_2 potentials are approximated as the sum of two Rg–I Lennard-Jones (LJ) potentials. The parameters such as polarizability, which is considered to be same for both ions and neutral species, used in their calculation are taken from different sources. So, any error in the values of parameters will be incorporated in the potential and hence will be reflected in the potential parameters. The vibrational frequency and anharmonicity constants are very much consistent with the available experimental values of Kiviniemi et al. [4, 5] and Böhling et al. [6].

For the T-shaped I_2–Xe isomer, results shown in Table 4, the experimental values of Kiviniemi et al. are available only for the equilibrium bond length r_e and the depth of the potential well (D_e or ε). The depth of the potential well estimated by potential method, and supermolecular approach is about 85 cm^{-1} lower than that reported by Kivineimi et al. It should be mentioned here that the values obtained by potential method and supermolecular approach for the dissociation energy (D_0) or depth of the potential well (D_e or ε) are almost same. It is important to note that if one calculates the experimental value for the dissociation energy (D_0) using the experimental value for the depth of the potential well, 421 cm^{-1} and the ZPE, about 126 cm^{-1}, the approximate experimental value for the dissociation energy would be 295 cm^{-1}, which is 10 cm^{-1} greater than that of its linear isomer. This implies that T-shaped isomer is more stable than linear isomer. But according to our calculations the latter is more stable than the former, which is reflected from their calculated ground state energies, well depths, and dissociation energies. At CCSD(T)/BS2 level, the linear isomer is 58.14 cm^{-1} more stable than the T-shaped isomer. Most of the spectroscopic constants are new.

The depth of the potential well calculated by the potential method is very sensitive to the value of van der Waals harmonic stretching force constant f_{11}. As seen from (4), the depth of the potential well (ε) is directly proportional to the square of the equilibrium bond length (r_e) and also to the harmonic force constant, the value of which is very small. So any error in the calculation of f_{11} makes an appreciable deviation in the value of the depth of the potential well. The small difference between the values of potential depth calculated by potential method and supermolecular approach is due to the small error in the calculation of f_{11}. This difference reduces to 2–4 cm^{-1} for the heavier complex.

Various dissociation channels and their dissociation energies for both the isomers of I_2–Rg (Rg = Kr and Xe) van der Waals complexes are displayed in Table 5. Both zero-point energy and BSSE correction are taken into

Table 4 Spectroscopic properties of T-shaped isomer of I_2–Xe van der Waals complex in its $^1\Sigma_g^+$ ground state

Spectroscopic properties	Method/basis set				Others
	MP2/BS1	MP2/BS2	CCSD(T)/BS1	CCSD(T)/BS2	Expt.
r_1 (I–Xe) (Å)	4.501	4.469	4.658	4.625	
r_2 (I–I) (Å)	2.678	2.663	2.706	2.687	
r_e (Å)	4.297	4.266	4.457	4.425	4.08[a]
D_0^p (cm^{-1})	306.0	337.3	174.3	208.3	
D_0^s (cm^{-1})	311.0	267.7	192.8	211.0	
D_e^p (cm^{-1})	439.2	473.4	295.9	334.1	421[a]
D_e^s (cm^{-1})	444.2	403.8	314.4	336.8	
B (cm^{-1})	0.01054	0.01066	0.00977	0.00991	
D_j (10^{-9} cm^{-1})	8.22	7.82			
ω_1 (cm^{-1})	21.1	22.0	16.7	17.8	
ω_2 (cm^{-1})	18.0	18.8	14.0	15.0	
ω_3 (cm^{-1})	227.2	231.7	212.4	218.6	
ω_3x_e (cm^{-1})	0.91	0.93			
f_{11} (mdyne/Å)	0.034	0.0372	0.0213	0.0244	
$f_{\theta\theta}$ (mdyne Å)	0.0244	0.0266	0.0148	0.0169	
f_{22} (mdyne/Å)	3.8594	3.9990	3.3734	3.5736	
f_{111} (mdyne/Å^2)	–0.0277	–0.0305	−0.0167	−0.0193	
ζ_{23}	0.88314	0.88243			
ζ_{21}	–0.46905	–0.46976			
ζ_{31}	–0.00781	–0.02539			

[a] Ref. [4]

Table 5 Dissociation energies for various channels for I_2–Rg ($^1\Sigma_g^+$) van der Waals complexes at CCSD(T)/BS2 level

Dissociation channels	Dissociation energy (cm^{-1})			
	Linear		T-shape	
	Rg = Kr	Rg = Xe	Rg = Kr	Rg = Xe
Rg (^{1}S) + I_2 ($^1\Sigma_g^+$)	188.7	281.6	159.0	211.0
RgI ($^2\Sigma_g^+$) + I (^{2}P)	12,214.4	11,722.5	12,184.8	11,673.0
Rg (^{1}S) + I (^{2}P) + I (^{2}P)	12,401.4	11,999.2	12,371.7	11,949.7

account to calculate the dissociation energies. Among the three possible channels, the first dissociation channel (Rg + I_2) is energetically most favorable, as its energy is calculated to be the lowest. The third dissociation channel (Rg + I + I) with highest dissociation energy is least favorable among the three. As T-shaped isomer is less stable than linear isomer of the van der Waals complexes, for all dissociation channels, the dissociation energies of the former are less than those of the latter. The T-shaped isomers dissociate faster than the linear isomers.

4 Conclusions

The spectroscopic properties of I_2–Kr and I_2–Xe have been studied in detail using MP2 and CCSD(T) methods in conjunction with correlation-consistent triple-ζ and quadruple-ζ quality basis sets. The effect of electron correlation has been taken into account properly in this calculation. The spectroscopic constants calculated at CCSD(T)/BS2 level are very much consistent with the existing experimental values. To remove discrepancy between various theoretical values and experimental results, we have calculated the ZPE corrected dissociation energy (D_0) and ZPE uncorrected dissociation energy (D_e) or depth of the potential well (ε) at CCSD(T)/BS2 level using both potential method and supermolecular approach. The dissociation energies obtained by the two methods are very consistent. For most of the complexes, the dissociation energy as well as depth of the potential well obtained by supermolecular approach agrees better with the experimental values. For linear isomer and T-shaped isomers of I_2–Kr complex, the calculated dissociation energy and well depth reproduce the experimental values of Kiviniemi et al. For linear and T-shaped isomers of I_2–Xe complex, our calculation supports the experimental values of Kiviniemi et al. and Böhling et al. Various dissociation channels have been explored for these complexes. Among three possible dissociation channels, the first one, Rg + I_2 channel is energetically most favorable and the third one, Rg + I + I is the least.

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